

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

R&T CODE: 4133032

Robert J. Nowak

TECHNICAL REPORT NO. 103

Template Synthesis of Graphitic Nanotubules

by

Ranjani V. Parthasarathy, K. L. N. Phani and Charles R. Martin

Prepared for publication

in

Advanced Materials



Department of Chemistry  
Colorado State University  
Ft. Collins, CO 80523

July 17, 1995

Reproduction in whole or part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited

DTIC QUALITY INSPECTED 5

19950720 062

36K

## REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE July 17, 1995	3. REPORT TYPE AND DATES COVERED Interim	
4. TITLE AND SUBTITLE Template Synthesis of Graphitic Nanotubes			5. FUNDING NUMBERS Contract # N00014-82K-0612	
6. AUTHOR(S) Ranjani V. Parthasarathy, K. L. N. Phani and Charles R. Martin				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dr. Charles R. Martin Department of Chemistry Colorado State University Fort Collins, CO 80523			8. PERFORMING ORGANIZATION REPORT NUMBER  ONR TECHNICAL REPORT #103	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) We describe a method for preparing monodisperse graphitic nanotubes. These tubules are prepared by synthesizing polyacrylonitrile (PAN) from the monomer, within the pores of a porous alumina template membrane. Because the membrane used has cylindrical pores of uniform diameter, monodisperse PAN tubules are obtained. The PAN tubules are then heated to affect graphitization of the PAN.				
14. SUBJECT TERMS  Nanomaterials, graphitic tubules			15. NUMBER OF PAGES 12	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT	

## TEMPLATE SYNTHESIS OF GRAPHITIC NANOTUBULES

Ranjani V. Parthasarathy, K.L.N. Phani, Charles R. Martin\*

Department of Chemistry  
Colorado State University  
Fort Collins, CO 80523

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

\*Corresponding author.

### Abstract

We describe a method for preparing monodisperse graphitic nanotubules. These tubules are prepared by synthesizing polyacrylonitrile (PAN) from the monomer, within the pores of a porous alumina template membrane. Because the membrane used has cylindrical pores of uniform diameter, monodisperse PAN tubules are obtained. The PAN tubules are then heated to affect graphitization of the PAN.

## Introduction

We have been exploring the concept of using the pores in nanoporous membranes as templates for preparing nanomaterials.<sup>[1,2]</sup> Because the membranes used have cylindrical pores of uniform diameter, monodisperse nanocylinders of the desired material are obtained in the pores of the template membrane. Depending on the material and the chemistry of the pore wall, these cylinders may be solid (a fibril) or hollow (a tubule). This is proving to be a very general route for preparing nanomaterials. We have used this method to prepare fibrils and tubules composed of metals, <sup>[4-6]</sup> electronically conductive polymers, <sup>[7-11]</sup> and semiconductors.<sup>[12]</sup> In this paper, we extend this template approach for preparing nanomaterials to carbons. We show that polyacrylonitrile (PAN) can be synthesized within the pores of an alumina template membrane to obtain ensembles of PAN nanotubules. These tubules can then be graphitized at high temperatures<sup>[13-15]</sup> to yield the corresponding graphitic nanotubules.

Wu and Bein have recently used a similar approach to obtain nanocarbon within the pores of a nanoporous zeolite<sup>[16]</sup>; however, their approach apparently yields solid graphitic fibers as opposed to the nanotubules obtained here. Nanotubules of the type described here might ultimately be interesting as analogs for the fullerene tubules.<sup>[17-18]</sup> In addition, we are interested in exploring the possibility of using ensembles of these tubules as anode materials in Li-ion batteries.<sup>[19]</sup> Ensembles of nanotubules are not possible using the previously published approach.<sup>[16]</sup> Finally, we have recently

learned that Kyotani et al, have used an alternative chemical synthesis for preparing graphitic nanotubules.[20]

### Experimental

*Tubule Synthesis.* Kyotani et al.[13,14] have developed a procedure for formation of highly-oriented graphite from PAN by using the 2-D space between montmorillonite lamellae as a template. We have used a similar procedure for chemically-synthesizing PAN within the pores of a commercially-available alumina filtration membrane (Anopore). The alumina membrane used had pores with diameters of ca. 260 nm and had a porosity of ca. 57 %<sup>[4]</sup>. The membrane was immersed into 50 mL of an aqueous solution that was 1.3 M in the monomer acrylonitrile. To this solution was added 25 mL of 15 mM ammonium persulfate and 25 mL of 20 mM sodium bisulfite; these species act as initiators for the polymerization of the acrylonitrile.<sup>[21]</sup> The solution was made acidic by adding a drop of 0.5 M sulfuric acid. All solutions were purged with nitrogen prior to and during polymerization.

The polymerization reaction was carried out at a temperature of 40° C for varying periods of time. During the polymerization period, polyacrylonitrile was produced from the monomer and deposited on the pore walls and on both membrane faces. Because PAN deposited on the pore walls, a tubule of PAN was obtained within each pore. After the desired polymerization time, the membrane was removed from the polymerization bath, and the PAN that deposited on the membrane faces was removed. This was accomplished by polishing both faces with alumina powder. The membrane was then ultrasonicated in water to remove the alumina

powder. After this polishing procedure, the only PAN remaining was the PAN tubules within the pores.

The membranes that contain PAN tubules within the pores are called PAN/ $\text{Al}_2\text{O}_3$  composite membranes. The PAN/ $\text{Al}_2\text{O}_3$  composite membrane was heated to  $250^\circ\text{C}$  in air for a period of 30 minutes; the membrane turned yellow due to cyclization of the PAN tubules.[22] The membrane was then heated for 30 min. in Ar at  $600^\circ\text{C}$ , after which the membrane appeared grayish-black, due to graphitization of the PAN.[22] The membranes that have been heat-treated in this way are designated Graph/ $\text{Al}_2\text{O}_3$  composite membranes.

*Electron microscopy.* Scanning electron microscopic (SEM) images of the graphitic tubules produced were obtained as follows: One face of the Graph/ $\text{Al}_2\text{O}_3$  composite membrane was coated with a thick (ca. 3 mm) film of Torrseal epoxy. The Torrseal was cured by heating at  $160^\circ\text{C}$  for one minute. The other face of the Graph/ $\text{Al}_2\text{O}_3$  composite was then repeatedly rinsed in 1M NaOH to dissolve the alumina membrane. Dissolution of the alumina membrane yielded an ensemble of the graphitic tubules that protrude from the substrate Torrseal surface. The tubules were sputtered with a thin film of gold and imaged with a Phillips 505 electron microscope.

*Infrared Spectroscopy.* IR spectra of both the PAN/ $\text{Al}_2\text{O}_3$  and Graph/ $\text{Al}_2\text{O}_3$  composites were obtained by conducting simple transmittance mode experiments on the membranes. A Mattson Galaxy FTIR was used.

## Results and Discussion

*Infrared Spectroscopy.* IR spectra of the PAN/Al<sub>2</sub>O<sub>3</sub> composite membrane show a band at 2243 cm<sup>-1</sup> due to the nitrile group of the PAN (Figure 1, upper spectrum). This peak is absent in the Graph/Al<sub>2</sub>O<sub>3</sub> spectrum indicating cyclization<sup>[22]</sup> of the PAN tubules (Figure 1, lower spectrum). The broad absorption at ca. 1650 cm<sup>-1</sup> in Figure 1 is due to the alumina template membrane.

*Scanning electron microscopy.* SEM images of template-synthesized graphitic tubules (after dissolution of the alumina membrane) are shown in Figure 2. These images clearly show that tubular structures are formed from this template synthetic method (Figure 2A). Note that the tubules obtained are ca. 50 μm long (Figure 2B); this corresponds to the thickness of the template membrane. As indicated in Figure 2A, these tubules can be made to stand up from a substrate surface like the bristles of a brush. This indicates that the tubules have good mechanical strength and are not broken along the tubule length. Indeed, these tubules show no visible signs of mechanical damage even though they have been ultrasonicated and exposed to strong base.

## Conclusions

The images shown in Figure 2 were obtained by growing PAN for a period of 10 minutes. By controlling the polymerization time, it is possible to control the wall thickness of the tubes. Thicker walls are obtained after longer polymerization. Put another way, by varying the polymerization time, it is possible to vary the inside diameter of the tubules obtained. The outside diameter of the tubules can be varied by varying the diameter of the pores in the



alumina template membrane. We have prepared membranes of this type with a wide variety of pore diameters.<sup>[1]</sup> The smallest pores we have prepared to date have diameters of ca. 8 nm<sup>[1]</sup> and we believe that even smaller pores are possible. In addition, the length of the tubule obtained can be varied by conducting syntheses of this type in template membranes of different thicknesses. Finally, our ability to prepare high density ensembles of tubules that protrude from a substrate surface (Figure 2A) could be useful in a variety of possible applications, including bioencapsulation<sup>[23]</sup> and Li-ion batteries.<sup>[19]</sup>

**Acknowledgments.** We would like to thank Vinod Menon for his valuable assistance and suggestions. This work was supported by the Office of Naval Research.

### References

1. C.R. Martin, *Science*. **1994**, 266, 1961.
2. C.R. Martin, *Acc. Chem. Res.* **1995**, 28, 61.
3. C.J. Brumlik, C.R. Martin, *J. Am. Chem. Soc.* **1991**, 113, 3174.
4. C.A. Foss, M.J. Tierney, C.R. Martin, *J. Phys. Chem.* **1992**, 96, 9001.
5. V. Menon, C.R. Martin, *Anal. Chem.* **1995**, in press.
6. N. Matsuhiko, V. Menon, C.R. Martin, *Science*, **1995**, in press.
7. Z. Cai , C.R. Martin , *J. Am. Chem. Soc.* **1989**, 111, 4138.
8. C.R. Martin , *Adv. Mater.* **1991**, 3, 457.
9. Z. Cai , J. Lei , W. Liang , V. Menon , C.R. Martin, *Chem. Mater.* **1991**, 3, 960.
10. C.R. Martin, R. Parthasarathy, V. Menon, *Synth. Met.* **1993**, 55, 1165.
11. R.V. Parthasarathy, C.R. Martin, *Chem. Mater.* **1994**, 6, 1627.
12. J.D. Klein, R.D. Herrick II, D. Palmer, M.J. Sailor, C.J. Brumlik, C.R. Martin, *Chem. Mater.* **1993**, 5, 902.
13. T. Kyotani, N. Sonobe, A. Tomita, *Nature*, **1988**, 331, 331.
14. N. Sonobe, T. Kyotani, Y. Hishiyama, M. Shiraishi, A. Tomita, *J. Phys. Chem.* **1988**, 92, 7029.
15. P. Enzel, J.J. Zoller, T. Bein, *J. Chem. Soc. Chem. Commun.* **1992**, 633.
16. C.G. Wu, T. Bein, *Science*, **1994**, 266, 1013.
17. S. Iijima, *Nature*, **1991**, 354, 56.
18. T.W. Ebbesen, P.M. Ajayan, *Nature*, **1992**, 358, 220.

19. K. Sato, M. Noguchi, A. Demachi, N. Oki, M. Endo, *Science*, **1994**, 264,556.
20. T. Kyotani, Li-fu Tsai, A. Tomita, submitted for publication.
21. H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, J.I. Kroschwitz (Ed.), *Encyclopedia of Polymer Science and Engineering*, John Wiley, Vol 1, p 443.
22. J.I. Kroschwitz, M.H. Grant (Ed.), *Encyclopedia of Chemical Technology (Kirk-othmer)*, John Wiley, fourth edition, Vol 5, Pp 1-11.
23. R.V. Parthasarathy, C.R. Martin, *Nature*, **1994**, 369, 298.

### Figure Captions

Figure 1. IR spectra for PAN/ $\text{Al}_2\text{O}_3$  (upper) and Graph/ $\text{Al}_2\text{O}_3$  (lower) membranes.

Figure 2. Scanning electron microscopic images of the graphitic tubules obtained.

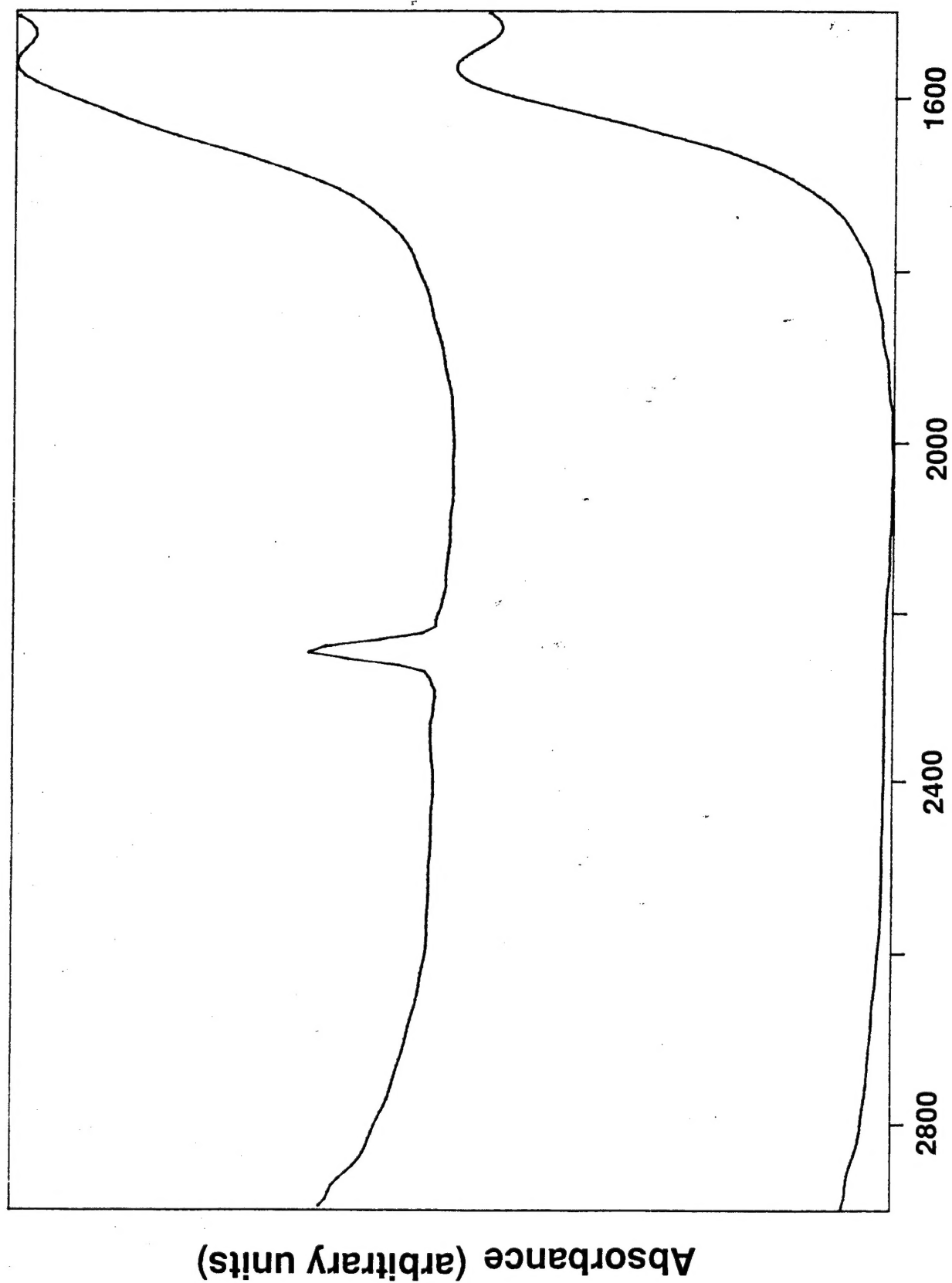


Figure 1

A.



B.



Figure 2